Preparation of Nano-Crystalline $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ by Solid-State Method

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$LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ has been synthesized at 150 °C using the solid-state method. A Li/$LiFeO_2$ cell as reported previously exhibited a large capacity decline until 15 cycles. To obtain a good cycleability of $LiFeO_2$, Co and Cl ions substituted some Fe and O atoms of the $LiFeO_2$ structure. $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ showed small lattice parameters compared with those of $LiFeO_2$. This material showed a good cycleability with fairly a high discharge capacity of over 134 mAh/g at high current density.

The commercial lithium battery with high energy density and good cycle life has been studied as a power source for portable electronics. Many research groups have investigated various cathode materials for the lithium secondary batteries such as a layered oxide; $LiMO_2$ (M = Co, Ni, Mn, Fe ⋯).[1–3]

$LiFeO_2$ has many advantages over these layered cathode materials because it is nontoxic and contains the most abundant metal in the world. It is well known that $LiFeO_2$ has different forms, i.e., the α-, β-, and γ-forms, due to the synthetic conditions and synthetic methods. The α-$LiFeO_2$ is a cubic unit cell of space group Fm3m, the β-$LiFeO_2$ (monoclinic, C2/c) is formed by an intermediate phase during the ordering process. The γ-$LiFeO_2$ (tetragonal, $I4_1$/amd) is obtained by reducing the symmetry from cubic to tetragonal by ordering the Li^+ and Fe^{3+} ions at octahedral sites.[4–6]

Kanno et al. found that the corrugated layered structure type $LiFeO_2$ was electrochemically active during the lithium insertion/extraction reaction.[4] They noticed one interesting point that orthorhombic $LiMnO_2$ using LiOH and γ-MnOOH, which has a structure similar to the conjugated $LiFeO_2$, was successfully synthesized by an ion exchange method at low temperature.[7] They succeeded in synthesizing $LiFeO_2$ using the H^+/Li^+ ion exchange reaction from γ-FeOOH at a reaction temperature of 100 to 500 °C. Although this Li/$LiFeO_2$ cell exhibited a fairly high initial discharge capacity of about 100 mAh/g, it shows a large capacity decline due to the cationic disorder in the voltage region of 4.2 and 1.5 V.

Tabuchi et al. reported many interesting results for all types of $LiFeO_2$ compounds. They successfully adopted a new synthetic process, the hydrothermal method, for the $LiFeO_2$ system.[5] Many kinds of starting materials (α-FeOOH, $Fe(NO_3)_3$, LiOH, NaOH, and KOH) at various Li/Fe (1–50) ratios were distilled in a Teflon beaker and hydrothermally treated at 230 °C in an autoclave. Although the α-$LiFeO_2$ derivatives were successfully obtained from α-FeOOH and LiOH by a one-step method, the cycling performance of the α-$LiFeO_2$ compound was very poor (5–10 mAh/g) in the range 4.5 to 1.5 V.

Recently, Sakurai et al.[6] reported a new result that the corrugated $LiFeO_2$, which is synthesized by a H^+/Li^+ ion exchange, could be easily obtained at low temperature when alcohol used as a reaction medium in the synthetic process.

From a review of previous studies, we found that almost all $LiFeO_2$ were obtained using a complex reaction mechanism. It needed a long reaction time or other reaction steps against the conventional solid-state method. Moreover, almost $LiFeO_2$ using these methods were unsatisfactory as a practical cathode material. Therefore, we report here a new type of orthorhombic $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ material with good cycling performance using a solid-state reaction at low temperature (150 °C).

$LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ was synthesized using $LiOH\cdot H_2O$, γ-FeOOH, and $CoCl_2\cdot 6H_2O$ by conventional solid-state method. The stoichiometric amount of each material was grounded and calcined at 150 °C for 15 h in Ar atmosphere in the box furnace. The contents of Li, Co, and Fe in the resulting material were analyzed with atomic absorption spectroscopy (AAS, AA-6200, Shimadzu, Japan) by dissolving the powder in the dilute nitric acid. The content of chlorine was measured by ion chromatography (IC, DX-120, DIONEX, Japan). The powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) using CuKα radiation was employed to identify the crystalline phase of the synthesized material. The particle morphology and energy dispersive X-ray spectrometer (EDX) of powder was observed using a scanning electron microscope (SEM, S-4000, Hitachi Co., Japan). The electrochemical tests were performed using CR2032 coin-type cells. The cells were assembled as detailed elsewhere.[8] The cycling was performed at a current density of 0.4 mA/cm^2 with a cut-off voltage of 1.5–4.5 V.

To synthesize Co-doped $LiFeO_2$ ($LiFe_{1-x}Co_xO_{2-y}Cl_y$) by a solid-state reaction, two mixtures of the LiOH, γ-FeOOH, and $CoCl_2$ starting materials were thoroughly ground for 20 min in a mortar. One was calcined in a ceramic boat without pressing; the other was pressed at a 300 kg/cm^2 pressure into a 20 mm diameter pellet to improve the reactivity between the particles of the precursor. Figure 1 shows X-ray diffraction patterns (XRD) of the raw γ-FeOOH, $LiFeO_2$, and the two Co-doped $LiFeO_2$ which were calcined at 150 °C for 15 h in an Ar atmosphere. Figure 1(b) shows a very similar XRD pattern when compared to the γ-FeOOH. It seems to have failed to form an orthorhombic structure, although there are some differences to that of the original γ-FeOOH, which resulted from the reaction with lithium hydroxide at 80 °C. On the other hand, Figure 1(c) and (d) display major orthorhombic patterns in the XRD diagram. $LiFeO_2$ was consisted of 100–200 nm sized needle-type particles and an orthorhombic phase (a = 4.0 Å, b = 3.0 Å, and c = 6.1 Å) with a small amount of β-$LiFe_5O_8$ (a = 8.3 Å) phase. The main differences between $LiFeO_2$ and Co-doped $LiFeO_2$ in the XRD are the concrete splits between the (102) and (110) peaks and between the (012) and (200) peaks. It means that doped ions were successfully substituted into the $LiFeO_2$ structure and increased

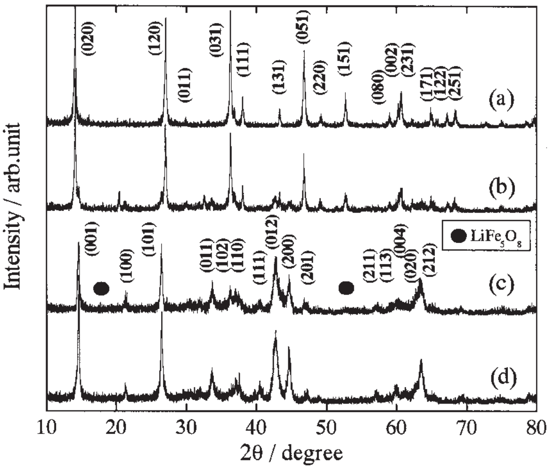

Figure 1. XRD patterns of (a) γ-FeOOH (b) $LiFeO_2$ without pelletizing (c) $LiFeO_2$ (d) $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$.

the crystallinity of original $LiFeO_2$ material. We found that the pelletizing played an important role in accelerating the slow reaction of lithium, cobalt, and γ-FeOOH particles, because the rate of the surface reaction of starting materials slowly occurred at a low temperature.

The EDX analysis suggested one more interesting fact to us, which the presence of chloride ion in the Co starting material. In general, many starting materials with halogen elements have a lower melting point ($CoCl_2{\cdot}6H_2O = 86\,^\circ C$) and boiling point than those of other elements. It promotes the easy evaporation of the halide ions in the material which was calcined at high temperature. This leaded to detecting only a small amount of halide ions or being undetectable by instrumental analysis. This indication was already reported for other lithium oxide materials.[9,10] However, the Co-doped $LiFeO_2$ in this research had the high possibility of chlorine remaining on/in the particles because this material was synthesized at low temperature (150 °C). The EDX image of the Co-doped $LiFeO_2$ exhibited a clear chlorine peak along with other elements. To investigate the amount of chlorine ion in this material, ion chromatography measured the chloride ion content. From the above analyses, it was concluded that the composition of the Co-doped $LiFeO_2$ material should be $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$.

Figure 2(a) shows the charge/discharge curves for Li/$LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ system. The test condition was a current density of 0.4 mA/cm^2 between 4.5 and 1.5 V. The Li/$LiFeO_2$ cell showed almost the same cycling patterns compared with those of other groups.[4,6] Li/$LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ cell also exhibited a similar cycle curve in the first charge as like as Li/$LiFeO_2$ cell. However, the first discharge curve of this cell abruptly decreased below 3.7 V and displayed a unique voltage plateau in the 3.5–3.3 V region. This plateau decreased from the second cycle, but it still remained at the 25th cycle. This indication was first reported here and we suggest it can be one important characteristic of the $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ compared with that of $LiFeO_2$.[4,6] In previous reports,[4] Li/$LiFeO_2$ cell exhibited a fairly good cycle performance in the early stage, but, the long-term cycling performance was not presented clearly, maybe because of the poor cycle performance after 15th cycle. However, the Li/$LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ cell showed not only a high initial capacity (134 mAh/g), but also a stable cycle behavior at high current density (0.4 mA/cm^2). The cycle retention rate was 80% after 25 cycles. Moreover, this cell exhibited no abrupt capacity drop after 13 cycles as shown in Figure 2(b).[11] This means that doped Co and Cl ion may affect the structure of the $LiFeO_2$ during the synthesis process and change the electrochemical properties of the parent $LiFeO_2$ material. We also suggest that the main reason for the improved cycle performance of $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ resulted from small lattice constants ($a = 4.00$ Å, $b = 2.96$ Å, and $c = 6.06$ Å) and small nano-particles of about 50–100 nm. These values were smaller than those of $LiFeO_2$ in other previous reports.[4,6,11] However, we still have no idea why $LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$ has small lattice constants, even though, the substituted Co^{2+} and Cl^- ions in the $LiFeO_2$ structure have a larger ionic radii than Fe^{3+} and O^{2-} ions. A more detailed discussion about the crystallographic properties and capacity loss mechanism will be reported elsewhere.

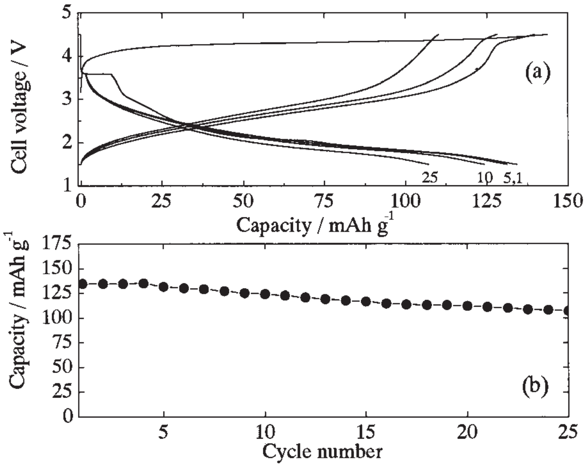

Figure 2. (a) Charge/discharge curves (b) specific discharge capacity for Li/$LiFe_{0.97}Co_{0.03}O_{1.95}Cl_{0.05}$.

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